

Chemistry of Epoxy Compounds. XII.¹ Co-oxidation of Aldehydes and Oleic Acid, Methyl Oleate or Oleyl Alcohol

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In an early paper,² we described the preparation of 9,10-epoxystearic acid in 70–80% yield by the ultraviolet light-catalyzed cooxidation of benzaldehyde and oleic acid with air in acetone solution. Perbenzoic acid was undoubtedly the oxidizing agent, although it was not isolated.³ This paper describes an extension of the cooxidation technique in which benzaldehyde, acetaldehyde or butyraldehyde was employed as the source of the intermediate peracid, and oleic acid, methyl oleate or oleyl alcohol was the unsaturated substance epoxidized.

Cooxidation of benzaldehyde and methyl oleate gave only about 40% yields of methyl 9,10-epoxystearate. The lower yield of methyl 9,10-epoxystearate, compared to that of 9,10-epoxystearic acid,² can probably be attributed to unavoidable loss of product during isolation. The even lower yield (20%) of 9,10-epoxyoctadecanol in the cooxidation of oleyl alcohol and benzaldehyde, cannot yet be explained. During the reaction, however, it was observed that the gain in weight of the reaction mixture far exceeded that which could be accounted for by acidic, peroxidic or epoxy components formed. Oleyl alcohol probably combines with oxygen or other components of the reaction mixture to form compounds of unknown structure.

In cooxidations with aliphatic aldehydes, good conversion of aldehydes to the corresponding aliphatic acids (50–70%) and low yields (20% or less) of 9,10-epoxystearic acid were obtained. There is little doubt that a chain reaction occurs and a peracid intermediate⁴ is formed in these reactions, but preferential oxidation of excess aldehyde may account for the low yields.

Experimental

Starting Materials.—Pure oleic acid, methyl oleate and oleyl alcohol were obtained by a previously published procedure.⁵ Benzaldehyde, b. p. 74° at 20 mm. and acid number below 1, was obtained from Eastman Kodak Co. chlorine-free grade by successive washing with 5% aqueous sodium carbonate, 5% sodium chloride and then with water, followed by drying over anhydrous calcium sulfate and distillation in an all-glass apparatus. These operations were conducted in an oxygen-free atmosphere. n-

Butyraldehyde, b. p. 73.5° and acid number below 1, was obtained by fractional distillation of the Eastman Kodak Co. purest grade in an oxygen-free atmosphere. Acetaldehyde, acid number 6, was the Eastman Kodak Co. purest grade and was used without further purification. Acetone was obtained by fractional distillation of the technical grade.

Cooxidation of Benzaldehyde and Methyl Oleate.—A solution consisting of 106 g. (1.0 mole) of benzaldehyde, 30 g. (0.1 mole) of 95% methyl oleate (containing 4% of saturated esters and 1% of methyl linoleate) and 180 ml. of acetone was cooxidized at 23–26° for twenty hours with dry air while the solution was being irradiated with ultraviolet light, as described previously.² It was not feasible to continue the cooxidation for more than twenty hours because of crystallization of benzoic acid in the fritted discs. The acetone solution was then cooled to –60° and the white precipitate which formed was filtered and freed of acetone. The product, which was a liquid at room temperature, was washed with 10% aqueous sodium bicarbonate, then with water, and finally dried over anhydrous calcium sulfate and filtered. The residual oil weighed 13.3 g. (42% yield) and consisted mainly of methyl 9,10-epoxystearate. Calcd. for oxirane oxygen, 5.09; sapon. equiv., 312.5. Found: oxirane oxygen, 4.33%; sapon. equiv., 311.3.

Cooxidation of Benzaldehyde and Oleyl Alcohol.—Repetition of the above experiment with 28.8 g. (0.1 mole) of 99% oleyl alcohol instead of methyl oleate, and crystallization of the reaction mixture at –65°, yielded 52 g. of crude product (acid number 241). This was washed acid-free with 6 N aqueous sodium hydroxide. The alkali-insoluble portion was a mushy solid (19 g.) having an oxirane oxygen content of 3.45% (calcd. 5.63). Recrystallization from ethyl acetate and then diethyl ether yielded 6 g. (21% yield) of impure 9,10-epoxyoctadecanol, m. p. 42–55° (lit.² 54°), and oxirane oxygen, 4.66%.

The aqueous, alkaline solution was acidified while hot, filtered, and cooled to room temperature, yielding 14 g. of benzoic acid, m. p. 122°.

Cooxidation of Acetaldehyde and Oleic Acid.—Twenty-eight grams (0.1 mole) of oleic acid, 44 g. (1.0 mole) of acetaldehyde and 240 ml. of acetone were cooxidized at 0–5° for twenty-four hours while the solution was irradiated with ultraviolet light.² The reaction solution was washed several times with water, and the residual oil was recrystallized from acetone at –25° yielding 4 g. (13% yield) of 9,10-epoxystearic acid, m. p. 50–52° (lit.,² 59°). Oxirane oxygen: calcd., 5.36; found, 4.59. Neutralization equivalent: calcd., 298.5; found, 292.5. Approximately 1/3 mole of acetic acid was formed during cooxidation.

Cooxidation of Butyraldehyde and Oleic Acid.—Twenty-eight grams (0.1 mole) of oleic acid, 72 g. (1.0 mole) of butyraldehyde and 195 ml. of acetone were cooxidized for 24 hours at 5° while the solution was irradiated with ultraviolet light.² The reaction mixture was worked up as described in the preceding experiment, yielding 6 g. (20% yield) of 9,10-epoxystearic acid, m. p. 50–53°. Oxirane oxygen, 4.56; neutralization equivalent, 299.2. Approximately 2/3 mole of butyric acid was formed during cooxidation. When the reaction was conducted at 30–50°, substantially the same yield of 9,10-epoxystearic acid but larger quantities of butyric acid were obtained. In the absence of ultraviolet radiation only about 1 g. of 9,10-epoxystearic acid was isolated.

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(6) Swern, Findley, Billen and Scanlan, *Anal. Chem.*, **19**, 444 (1947).

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(1) See THIS JOURNAL, **72**, 3364 (1950), for the previous paper in this series.

(2) Swern, Findley and Scanlan, *ibid.*, **66**, 1925 (1944).

(3) Jorissen and van der Beek, *Rec. trav. chim.*, **45**, 245 (1926), **46**, 42 (1927); van der Beek, *ibid.*, **47**, 286 (1928); Raymond, *J. chim. phys.*, **28**, 480 (1931).

(4) See Swern, *Chem. Reviews*, **45**, 1 (1949), for the numerous literature references.

(5) Swern, Knight and Findley, *Oil and Soap*, **21**, 133 (1944).